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### (54) METHOD FOR MANUFACTURING HEAT-RESISTANT SHEET AND MOLDED BODY OF POLYETHYLENE TEREPHTHALATE POLYESTER

#### (57)Abstract:

PROBLEM TO BE SOLVED: To provide heat-resistant sheets and molded bodies useful in such fields as everyday items, civil engineering and construction materials, electronic and electric members and automotive members by using polyethylene terephthalate (PET) polyesters modified to a long chain branched structure and block-copolymerized with another polyester or a polyolefin.

SOLUTION: A mixture comprising (a) 100 pts.wt. PET polyester, (b) 0-100 pts.wt. other polyester or polyolefin containing carboxylic acid groups, (c) 1-15 pts.wt. master batch of a mixture with 0-75/100-25 weight ratio of at least a trifunctional epoxy compound/bifunctional epoxy compound as a bonding agent and (d) 0.25-10 pts.wt. master batch of a composite body of organic acid metal salts as a bonding catalyst, is modified to a long chain branched structure with a fast crystallization speed by a reaction extrusion method to prepare a block copolymer with a melt viscosity increased at least 10 times of a conventional PET with a linear structure.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1]An A Ingredient:(1) melt flow rate (the JIS method: 280 \*\*, 2.16 kg of load) 40-200g/polyethylene terephthalate system polyester a:100 weight section for 10 minutes, (2) As a binding material. the binding material masterbatch f:1-10 which comprises d:10 to mixture 50 weight section of c:75 to 0 % of the weight of compounds and e:base 100 weight section which contain three or more epoxy groups in b:25 to 100 % of the weight of compounds which contain two epoxy groups in intramolecular, and intramolecular -- repeatedly -- a quantity part. (3) A mixture which comprises i:0.25 to catalyst master batch 10 weight section which comprises the metal salt g:5-15 of organic acid, and h:base 100 weight section as a ligation reaction catalyst, B1 ingredient : A melt flow rate (the JIS method: 280 \*\*, 2.16 kg of load) 200g/zero to aromatic system polyester 100 weight section for 10 or less minutes, By carrying out a homolytic reaction with a reaction extrusion method, carrying out deaeration drying by a vacuum system below at  $13.3 \times 10^3$  Pa, while carrying out melting at temperature more than the melting point, consider it as the melt flow rate 60g/a block copolymer for 10 or less minutes, and it is fabricated on a sheet, A transparent heat-resistant sheet of polyethylene terephthalate system polyester and a manufacturing method of a Plastic solid using a hot-forming object.

[Claim 2]An A Ingredient:(1) melt flow rate (the JIS method: 280 \*\*, 2.16 kg of load) 40-200g/polyethylene terephthalate system polyester a:100 weight section for 10 minutes, (2) As a binding material. f:1 to binding material masterbatch 10 weight section which comprises d:10 to mixture 50 weight section of c:75 to 0 % of the weight of compounds and e:base 100 weight section which contain three or more epoxy groups in b:25 to 100 % of the weight of compounds which contain two epoxy groups in intramolecular, and intramolecular, (3) A mixture which comprises i:0.25 to catalyst master batch 10 weight section which comprises the metal salt g:5-15 of organic acid, and h:base 100 weight section as a ligation reaction catalyst, B-2 ingredient : a melt flow rate (the JIS method: 280 \*\*, 2.16 kg of load) zero to polyolefine

100 weight section which contains one or more carboxylic acid groups in 200g/intramolecular for 10 or less minutes, By carrying out a homolytic reaction with a reaction extrusion method, carrying out deaeration drying by a vacuum system below at  $13.3 \times 10^{-3}$  Pa, while carrying out melting at temperature more than the melting point, consider it as the melt flow rate 60g/a block copolymer for 10 or less minutes, and it is fabricated on a sheet, An opaque heat-resistant sheet of polyethylene terephthalate system polyester and a manufacturing method of a Plastic solid using a hot-forming object.

[Claim 3] A block copolymer manufactured by a method indicated in any 1 paragraph of claims 1-2 is once pelletized, A heat-resistant sheet of polyethylene terephthalate system polyester and a manufacturing method of a Plastic solid fabricating on a sheet a mixture which comprises the 100 weight sections and 0.01 to lubricant 1 weight section, and making it a hot-forming object.

[Claim 4] The polyethylene terephthalate system polyester a Intrinsic viscosity 0.50 - polyethylene terephthalate of 0.90 dl/g, Polyethylene terephthalate system aromatic polyester, A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of claims 1-3 containing at least one or more sorts chosen from a group which consists of a polyethylene terephthalate system aromatic polyester mold-goods recycle thing, and a manufacturing method of a Plastic solid.

[Claim 5] The compound b which contains two epoxy groups in intramolecular as a binding material Ethylene glycol diglycidyl ether of an aliphatic series system, Polyethylene glycol diglycidyl ether, Alicyclic system hydrogenation bisphenol A diglycidyl ether. And a heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of claims 1-3 containing at least one or more sorts chosen from a group which consists of aromatic system bisphenol A diglycidyl ether and a manufacturing method of a Plastic solid.

[Claim 6] The compound c which contains three or more epoxy groups in intramolecular as a binding material. Trimethylolpropane triglycidyl ether of a \*\*\*\*\* system, glycerol triglycidyl ether, Epoxidized soybean oil, epoxidation linseed oil, heterocyclic triglycidyl isocyanurate, and aromatic system phenol novolak type epoxy resin, Cresol novolak type epoxy resin, A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of claims 1-3 containing at least one or more sorts chosen from a group which consists of screw resorcinol tetraglycidyl ether, and a manufacturing method of a Plastic solid.

[Claim 7] As the ligation reaction catalyst g, lithium salt of stearic acid or acetic acid, sodium salt, Potassium salt, magnesium salt, calcium salt, zinc salt, A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of claims 1-3 being the complexes containing at least two or more sorts chosen from a group which consists of manganese salt, and a manufacturing method of a Plastic solid.

[Claim 8] In B1 ingredient, (1) melt flow rate (the JIS method: 280 \*\*, 2.16 kg of load)

Polyethylene terephthalate which is not dried [ 200g/desiccation for 10 or less minutes, or ], Polybutylene terephthalate, cyclohexane dimethanol system copolycondensation polyester, A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of claims 1-3 containing at least one or more sorts chosen from a group which consists of reagin of a polyethylene terephthalate system mold-goods recycle thing and A ingredient, and a manufacturing method of a Plastic solid.

[Claim 9]B-2 ingredient is the polyolefine which contains one or more carboxylic acid groups in intramolecular, Polyethylene in which copolymerization of the ethylene system monomer containing a maleic anhydride or a carboxylic acid group was carried out, A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of claims 1-3 containing at least one or more sorts chosen from a group which consists of polypropylene, ethylene propylene copolymers, and those mixtures, and a manufacturing method of a Plastic solid.

[Claim 10]Manufacturing a block copolymer of the ingredient A, the ingredient B1, or ingredient B-2 with reaction equipment for launching. A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of claims 1-9 newly carrying out additional supply of the ingredient B1 or ingredient B-2 to a metallic mold, fabricating on two-sort two-layer, two sorts of three layers, or a multilayer sheet, and manufacturing a hot-forming object, and a manufacturing method of a Plastic solid.

[Claim 11]A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of claims 1-10, wherein roll temperature in extrusion molding of a sheet is 30-150 \*\*, and a manufacturing method of a Plastic solid.

[Claim 12]A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of claims 1-11, wherein a die temperature in sheet hot forming is 90-150 \*\*, and a manufacturing method of a Plastic solid.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the cheap heat-resistant sheet of heat-resistant polyethylene terephthalate system polyester heat-resistant [ transparent ] and opaque, and a Plastic solid which is equal to heating of the container in which heating restoration is possible, and a microwave oven.

[0002]

[Description of the Prior Art]In recent years, the demand to containers, such as tofu of an about 80-90 \*\* heatproof and fermented soybeans, the lunch container of the convenience store of an about 110-130 \*\* heatproof, etc. is increasing quickly as a container which is equal to heating of the container in which heating restoration is possible, and a microwave oven. Conventionally, polypropylene (PP), polystyrene (PS), polyethylene terephthalate (A-PET or C-PET), polybutylene terephthalate (PBT), and polycarbonate (PC) have been used as a raw material of those containers. These raw materials have merits and demerits about quality, a price, environmental suitability, etc. containing heat resistance. For example, although polypropylene (PP) is cheap and processability is good, it is a little inferior to transparency, and elution of stabilizer etc. is seen at an elevated temperature. The heat resistance of a microwave oven shall be about 120 \*\*. Although polystyrene (PS) is cheap and processability and transparency are good, the safety technical problem of a residual monomer occurs, it is slightly weak and it is supposed that modification may take place the heat resistance of a microwave oven as a lunch container at about 110 \*\*. Although polyethylene terephthalate (A-PET) is excellent in transparency, intensity, and environmental suitability, a price is a little high and it has a weak point from which whitening and embrittlement (C-PET-izing) by crystallization arise at about 120 \*\* of the heat-resistant temperature of a microwave oven. Although polyethylene terephthalate (C-PET) is excellent in heat resistance and environmental

suitability, since its fabricating operation is special and its price is opaque it is high and white, a use is limited (for example, for [ which is the heat-resistant temperature of about 220 °C ] microwave ovens). Although it has succeeded in the sheet and container of a 140 °C heatproof with the constituent which consists of 70 to polybutylene terephthalate (PBT) system resin 100 weight section, and 30 to polyethylene terephthalate (PET) system resin 0 weight section. Since there is more PBT than (for example, the No. 2553228 gazette) and PET, a price becomes high. Although polybutylene terephthalate (PBT) and polycarbonate (PC) are excellent in transparency, intensity, and heat resistance, since the raw material of a raw material is expensive, their price of sheets is very high, and they cannot satisfy demand again. [0003]The necessity for reuse of the used plastic collected from the factory production process or the general spending market is globally recognized from a viewpoint of saving resources and environmental protection in recent years. A lot of recovery reuse was being advanced positively, and cheap acquisition especially of a used pet's bottle, a film, a sheet, etc. called the half the price of general-purpose resin was attained. On the other hand, the molecular weight of the flake (debris) of the recovered PET bottle which a molecular weight falls, for example, a used recovery pet derives in large quantities as compared with a new article pellet is mostly reduced by half. Therefore, when only this is reused as base resin, molding workability is bad, a Plastic solid is weak, shock resistance is also inferior in it, and quality of the original PET bottle cannot be guaranteed. As a result, it becomes textiles, a low quality sheet, etc. which can be fabricated also with low molecular weight, but the use of the reuse is limited to the narrow range. Since PET system polyester of the quality of clear glass has a glass transition temperature as high as not less than 70 °C and it is inferior to cold brittleness (cold resistance) and shock resistance, exploitation of a new use is also difficult for it. On the other hand, although polyolefines, such as polyethylene and polypropylene, are used for a film, a sheet, a container, etc. in large quantities, it is known that rigidity and hardness are far inferior as compared with rigid PVC, PET system polyester, or polystyrene. [0004]As one of the methods of solving these problems, About the method of recovering and increasing, i.e., PET system polyester, a molecular weight, In order to compensate the method of recovering a molecular weight by solid phase polymerization, the method of making a chain elongation agent (binding material) and a polyester end group react, and increasing a molecular weight, and a mechanical property, the method of adding other resin, such as an elastomer, etc. are known. Using the compound which has a joint hand or functional groups, such as isocyanate, oxazoline, epoxy, an aziridine, and a carbodiimide, as a chain elongation agent (binding material) for increasing a molecular weight is proposed. However, the restrictions from reactivity, heat resistance, stability, etc. are strong, and that practical is limited. What is comparatively useful as for an epoxy compound, and blended the mono epoxy compound also in these (JP,57-161124,A), Although there were things (JP,7-166419,A, JP,48-

25074,B, JP,60-35944,B, etc.) which blended the diepoxy compound, there was a problem in reaction velocity, gel formation, melt viscosity, compatibility, thermal stability, the physical properties of a cast, etc. plentifully, and utilization was difficult.

[0005]The method of, carrying out melting mixing of the collected PET system polyester on the other hand with the epoxy resin of two functionality and sterically-hindered hydroxyphenyl alkyl phosphonate, and increasing the molecular weight of polyester is proposed (the Patent Publication Heisei No. 508776 [ eight to ] gazette). Although this method has comparatively early reaction velocity, the sterically-hindered hydroxyphenyl alkyl phosphonate to be used is expensive, and a technical problem remains in practicality in the food packing industry where the industry where the collection cycle expense of low cost is required, and safety are required. While this invention persons proposed previously, PET system polyester of a molecular weight concomitant use and the specific catalyst of a two functionality and polyfunctional epoxy compound, melting mixing, and the method (PCT WO98/44019) of carrying out a ligation reaction, The molecular weight and melt tension of this polyester are increased, and a fabricating-operation article has the slightly weak bottom (PCT WO00/20491) possible in foaming, and it is completely insufficient for an improvement of shock resistance and cold brittleness (cold resistance). For example, the sheet forming object which does not break at the low temperature of 20 thru/or 30 \*\* of minus, but, on the other hand, has 130 \*\* of heat resistance of 230 \*\* still more preferably preferably as materials for frozen foods is required.

[0006]Although the blending method which blends rubber, an elastomer, a soft metallocene system polyethylene copolymer, etc. with PET system polyester was also proposed, in those cases, compatibility was dramatically bad and there was a difficulty in the drying property of heat resistance, an elastic modulus, and a pellet, etc. On the other hand, although the blending method which blends PET system polyester with polyethylene or polypropylene is also proposed, deterministically, mixing nature and compatibility are bad and have not put a part in practical use except for a use. .While this invention persons proposed previously, PET system polyester of a molecular weight, and the polyolefine containing a carboxylic acid group according to concomitant use and the specific catalyst of a two functionality and polyfunctional epoxy compound. melting mixing and the polyolefine polyester block copolymer method (JP,2001-122955,A) which made carry out a ligation reaction and was manufactured have shock resistance and remarkable cold brittleness (cold resistance) by increase of the amount of polyolefines, although the grade improvement was carried out, Mixing nature and homogeneity were not necessarily enough, gel and a fish eye carried out the byproduction, molding workability was not enough, and \*\* was lacked, the surface of the sheet forming object became orange peel-like, when extreme, and it was insufficient as goods.

[0007]

[Problem(s) to be Solved by the Invention]Although what is necessary is just to use as a basic

material the recovered PET bottle and recovery pet sheet which can be obtained at the half the price of general-purpose resin in order to realize the cheap heat-resistant sheet and Plastic solid of an aforementioned problem, the molecular weight is falling and it does not become a good sheet. Therefore, it is required to use the amount of polymers. However, since a line structure generates by the conventional solid phase polymerizing method and the crystallization rate is as slow as a part order in the compressed air of the time of sheet forming, and a sheet, or the heating immobilization at the time of vacuum pressure sky shaping (heat setting), It is difficult to cost a molding cycle for a long time, and to realize a cheap heat-resistant sheet and Plastic solid. On the other hand, since A-PET sheet which does not carry out heating immobilization (heat setting) has a crystallization zone in about 120 \*\*, there is no heat resistance. An object of this invention is to provide the manufacturing method of the cheap heat-resistant sheet of heat-resistant polyethylene terephthalate system polyester heat-resistant [ transparent ] and opaque, and a Plastic solid which is equal to heating of the container in which heating restoration is possible, and a microwave oven.

[0008]

[Means for Solving the Problem]a result of having repeated research wholeheartedly this invention persons solving the above-mentioned technical problem -- the above-mentioned technical problem -- dramatic -- an improvement -- things are succeeded and it came to complete this invention. That is, a cheap recovery pet was used for a base of a raw material. It was considered as a sheet which adopted a masterbatch method reaction extrusion method which uses a binding material and a catalyst for the polymers quantification, and decreased a byproduction of gel or a fish eye dramatically at high speed. By using together a compound (three or more organic functions: T) which contains three or more epoxy groups at intramolecular to a compound (two organic functions: D) which contains two epoxy groups in intramolecular as a binding material, introduced a "long chain branching structure object", a T/D ratio was made to increase, and a crystallization rate was increased. This is presumed to be that on which a compound containing an epoxy group of three or more organic functions acts as "a crystallization nucleating additive of molecular size." Since a long chain branching structure object of this invention becomes possible [ increasing melt viscosity also by about 10 to 100 times by the "tangle effect" of a chain compared with the conventional line structure ], it serves as a compressed air or a sheet with little drawdown at the time of vacuum pressure sky shaping. By carrying out block copolymerization of the polyolefine (B-2) containing aromatic polyester (B1 ingredient) or carboxylic acid like a case of polyethylene terephthalate system polyester (a ingredient), In a compressed air of the time of sheet forming, and a sheet, or heating immobilization at the time of vacuum pressure sky shaping (heat setting), a crystallization rate was able to be synthetically brought forward for an order of a second. When it is a container in which heating restoration of tofu with a heat resistance of about 80-90 \*\*,

fermented soybeans, etc. is possible, heating immobilization (heat setting), It was able to carry out at about 90-100 \*\*, and, in the case of a lunch container isochore machine of a convenience store which is equal to heating of a microwave oven with a heat resistance of about 110-130 \*\*, was able to carry out at about 120-150 \*\*. As a result, it becomes possible to reach with See of heat-resistant polyethylene terephthalate system polyester heat-resistant [ transparent ] and opaque which is equal to heating of a container in which heating restoration is possible, and a microwave oven in this invention, and to improve the productivity of a Plastic solid, It came to complete a manufacturing method of a cheap heat-resistant sheet and a Plastic solid.

[0009]That is, this invention provides the following invention matter. To the 1st, it is an A ingredient:(1) melt flow rate (the JIS method: 280 \*\*). 2.16 kg of load 40-200g/a:polyethylene terephthalate system polyester 100 weight section for 10 minutes, (2) As a binding material. the binding material masterbatch f:1-10 which comprises d:10 to mixture 50 weight section of c:75 to 0 % of the weight of compounds and e:base 100 weight section which contain three or more epoxy groups in b:25 to 100 % of the weight of compounds which contain two epoxy groups in intramolecular, and intramolecular -- repeatedly -- a quantity part. (3) A mixture which comprises i:0.25 to catalyst master batch 10 weight section which comprises the metal salt g:5-15 of organic acid, and h:base 100 weight section as a ligation reaction catalyst, B1 ingredient : A melt flow rate (the JIS method: 280 \*\*, 2.16 kg of load) 200g/zero to aromatic system polyester 100 weight section for 10 or less minutes, By carrying out a homolytic reaction with a reaction extrusion method, carrying out deaeration drying by a vacuum system below at  $13.3 \times 10^3$  Pa, while carrying out melting at temperature more than the melting point, consider it as the melt flow rate 60g/a block copolymer for 10 or less minutes, and it is fabricated on a sheet, A transparent heat-resistant sheet of polyethylene terephthalate system polyester and a manufacturing method of a Plastic solid using a hot-forming object. To the 2nd, it is an A ingredient:(1) melt flow rate (the JIS method: 280 \*\*). 2.16 kg of load 40-200g/a:polyethylene terephthalate system polyester 100 weight section for 10 minutes, (2) As a binding material. f:1 to binding material masterbatch 10 weight section which comprises d:10 to mixture 50 weight section of c:75 to 0 % of the weight of compounds and e:base 100 weight section which contain three or more epoxy groups in b:25 to 100 % of the weight of compounds which contain two epoxy groups in intramolecular, and intramolecular, (3) A mixture which comprises i:0.25 to catalyst master batch 10 weight section which comprises the metal salt g:5-15 of organic acid, and h:base 100 weight section as a ligation reaction catalyst, B-2 ingredient : a melt flow rate (the JIS method: 280 \*\*, 2.16 kg of load) zero to polyolefine 100 weight section which contains one or more carboxylic acid groups in 200g/intramolecular for 10 or less minutes, By carrying out a homolytic reaction with a reaction extrusion method, carrying out deaeration drying by a vacuum system below at  $13.3 \times 10^3$  Pa, while carrying out

melting at temperature more than the melting point, consider it as the melt flow rate 60g/a block copolymer for 10 or less minutes, and it is fabricated on a sheet, An opaque heat-resistant sheet of polyethylene terephthalate system polyester and a manufacturing method of a Plastic solid using a hot-forming object. A block copolymer manufactured by a method indicated [ 3rd ] in any 1 paragraph of the above 1-2 is once pelletized, A heat-resistant sheet of polyethylene terephthalate system polyester and a manufacturing method of a Plastic solid fabricating on a sheet a mixture which comprises the 100 weight sections and 0.01 to lubricant 1 weight section, and making it a hot-forming object. The polyethylene terephthalate system polyester a to the 4th Intrinsic viscosity 0.50 - polyethylene terephthalate of 0.90 dl/g, Polyethylene terephthalate system aromatic polyester, A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of the above 1-3 containing at least one or more sorts chosen from a group which consists of a polyethylene terephthalate system aromatic polyester mold-goods recycle thing, and a manufacturing method of a Plastic solid. The compound b which contains [ 5th ] two epoxy groups in intramolecular as a binding material. Ethylene glycol diglycidyl ether of an aliphatic series system, polyethylene glycol diglycidyl ether, Alicyclic system hydrogenation bisphenol A diglycidyl ether. And a heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of the above 1-3 containing at least one or more sorts chosen from a group which consists of aromatic system bisphenol A diglycidyl ether and a manufacturing method of a Plastic solid. The compound c which contains [ 6th ] three or more epoxy groups in intramolecular as a binding material. Trimethylolpropane triglycidyl ether of a \*\*\*\*\* system, glycerol triglycidyl ether, Epoxidized soybean oil, epoxidation linseed oil, heterocyclic triglycidyl isocyanurate, and aromatic system phenol novolak type epoxy resin, Cresol novolak type epoxy resin, A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of the above 1-3 containing at least one or more sorts chosen from a group which consists of screw resorcinol tetraglycidyl ether, and a manufacturing method of a Plastic solid. To the 7th, as the ligation reaction catalyst g, lithium salt of stearic acid or acetic acid, Sodium salt, potassium salt, magnesium salt, calcium salt, zinc salt, A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of the above 1-3 being the complexes containing at least two or more sorts chosen from a group which consists of manganese salt, and a manufacturing method of a Plastic solid. To the 8th, B1 ingredient is (1) melt flow rate (the JIS method: 280 \*\*). 2.16 kg of load Polyethylene terephthalate which is not dried [ 200g/desiccation for 10 or less minutes, or ], Polybutylene terephthalate, cyclohexane dimethanol system copolycondensation polyester, A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of the above 1-3 containing at least one or more sorts chosen from a group which consists of reagent of a polyethylene terephthalate system mold-goods recycle thing and A ingredient, and a manufacturing method

of a Plastic solid. It is the polyolefine in which B-2 ingredient contains one or more carboxylic acid groups in the 9th at intramolecular, Polyethylene in which copolymerization of the ethylene system monomer containing a maleic anhydride or a carboxylic acid group was carried out, A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of the above 1-3 containing at least one or more sorts chosen from a group which consists of polypropylene, ethylene propylene copolymers, and those mixtures, and a manufacturing method of a Plastic solid. Manufacturing a block copolymer of the ingredient A, the ingredient B1, or ingredient B-2 with reaction equipment for launching to the 10th. A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of the above 1-9 newly carrying out additional supply of the ingredient B1 or ingredient B-2 to a metallic mold, fabricating on two-sort two-layer, two sorts of three layers, or a multilayer sheet, and manufacturing a hot-forming object, and a manufacturing method of a Plastic solid. A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of the above 1-10 characterized [ 11th ] by roll temperature in extrusion molding of a sheet being 30-150 \*\*, and a manufacturing method of a Plastic solid. A heat-resistant sheet of polyethylene terephthalate system polyester given in any 1 paragraph of the above 1-11 characterized by a die temperature in sheet hot forming being 90-150 \*\* the 12th, and a manufacturing method of a Plastic solid.

[0010]

[Embodiment of the Invention]In this invention, the polyethylene terephthalate (PET) in which aromatic saturated polyester a as a raw material prepolymer of A ingredient is globally mass-produced as PET system aromatic polyester, or its copolymer is mentioned. Polyethylene terephthalate (PET or a pet) is preferred. The intrinsic viscosity (IV value) of PET system aromatic polyester of this invention which was dissolved in 1,1,2,2-tetrachloroethane / phenol (1:1) mixed solvent, and was measured at 25 \*\* is 0.50 or more (this) dl/g. The JIS method, the temperature of 280 \*\*, and the melt flow rate (MFR) in load 2.16kgf correspond in about 210g/10 minutes or less. It is the same as below. A certain thing is preferred and it is more preferred that they are 0.60 or more (MFRs are about 130g/10 minutes or less) dl/g. Polymers quantification and a raise in melt viscosity are difficult also by this invention in intrinsic viscosity being less than 0.50 dl/g, and there is a possibility that the molding workability and physical properties in which the polyester polyethylene block copolymer obtained was not necessarily excellent cannot be given. Although the maximum in particular of intrinsic viscosity is not restricted, it is usually 0.80 dl/g (MFRs are about 45g/10 minutes or more) preferably 0.90 dl/g (MFRs are about 25g/10 minutes or more).

[0011]The flake or pellet of a PET bottle of the PET system polyester collected and collected in large quantities actually is used as a prepolymer in many cases. Usually, since the intrinsic viscosity which the PET bottle has is high in comparison, the intrinsic viscosity of a recovery

article is also high and, especially generally is 0.65 - 0.75 dl/g (MFRs are 100-55g/10 minutes) 0.60 to 0.80 dl/g (MFRs are 130-45g/10 minutes). Generally, although the flake of a recovered PET bottle is supplied in the paper bag article containing 20 kg, and the FUREKON article containing 600 kg, the amount of water content is usually a 3,000-6,000 ppm (0.3 to 0.6 % of the weight) grade. Of course, the skeleton flake of A-PET sheet collected from a vacuum pressure sky molding plant in large quantities is also preferred as saturated polyester of the raw material of this invention.

[0012]B1 ingredient of this invention is (1) melt flow rate (the JIS method: 280 \*\*). 2.16 kg of load The polyethylene terephthalate which is not dried [ 200g/the desiccation for 10 or less minutes, or ], The thing containing at least one or more sorts chosen from the group which consists of reagin of polybutylene terephthalate, cyclohexane dimethanol system copolycondensation polyester, a polyethylene terephthalate system mold-goods recycle thing, and A ingredient can be used.

[0013]The polyolefines which contain one or more carboxylic acid groups in the intramolecular of B-2 ingredient of this invention are the polyethylene in which copolymerization of the ethylene system monomer containing a maleic anhydride or a carboxylic acid group was carried out, an ethylene propylene copolymer, polypropylene, and those mixtures. The polyolefine which added a maleic anhydride and organic peroxide in polyethylene or polypropylene and in which the carboxylic acid group was introduced into it by pyrogenetic reaction processing can be used. The partial saponification thing of an ethylene alkyl acrylate copolymer can be used. As an example of a commercial item, for example, polyethylene of Japanese Polyolefine, Copolymers (lex pearl ET series: 190 \*\* MFRs 8-80g/10 minutes, the melting point of 70-98 \*\*, one content of alkyl acrylate - 10 % of the weight of numbers, several percent of the weight content of a maleic anhydride), such as alkyl acrylate and a maleic anhydride, can be used. the ADTEX series-P type (2-25g of 230 \*\* MFR/-- for 10 minutes.) of the polyolefine and the maleic anhydride graft copolymer of the company the melting point of 145-162 \*\*, and HD type (0.2-0.5g of 190 \*\* MFR/-- for 10 minutes.) The melting point of 130-135 \*\*, a LDPE type (190 \*\* MFRs 1.0-11g/10 minutes, melting point of 102-106 \*\*), and a LLDPE type (190 \*\* MFRs 1.0-5.5g/10 minutes, melting point of 110-122 \*\*) can be used.

[0014]The binding material of this invention is a compound containing the epoxy group of the number (d) which exceeds 3 by two pieces (b) and a case to intramolecular. Usually, as an example of the compound b which has an average of two epoxy groups in intramolecular, The polyethylene glycol diglycidyl ether of an aliphatic series system, polypropylene glycol diglycidyl ether, Tetramethylene glycol diglycidyl ether, 1,6-hexamethylene glycol diglycidyl ether, Neopentyl glycol diglycidyl ether, glycerin diglycidyl ether, Hydrogenation bisphenol A diglycidyl ether of an alicyclic system, hydrogenation isophthalic acid diglycidyl ester, 3,4-epoxycyclohexylmethyl 3,4-epoxy cyclohexane carboxylate, A bis(3,4-epoxycyclohexyl)horse

mackerel peat and diglycidyl hydantoin of a heterocyclic system, Diglycidyl oxy alkyl hydantoin and the bisphenol A diglycidyl ether of an aromatic system, The initial condensate of bisphenol A diglycidyl ether, diphenylmethane diglycidyl ether, terephthalic acid diglycidyl ester, isophthalic acid diglycidyl ester, diglycidyl aniline, etc. can be mentioned.

[0015]As an example of the compound c which has an average of three epoxy groups in intramolecular, Trimethylolpropane triglycidyl ether of an aliphatic series system, glycerol triglycidyl ether, Triglycidyl Paller of triglycidyl isocyanurate of a heterocyclic system, triglycidyl cyanurate, triglycidyl hydantoin, and an aromatic system or a metha- aminophenol can be mentioned. As the compound c which has an epoxy group of some interim number from an average of 2.1 or more pieces in diamino Feni RUMETAN and a tetraglycidyl ether screw aminomethyl cyclohexane division-into-equal-parts child, Phenol novolak epoxy resin, a cresolnovolak epoxy resin, a biphenyl dimethylene system epoxy resin (for example, heat-resistant epoxy resin NC-3000 series of Nippon Kayaku Co., Ltd.), etc. can be mentioned. As other examples, about 2.2, 3.6 and 3.8, and 5.5 things are marketed on the average from the Dow Chemical Co. by the epoxy group of intramolecular, and these can be used.

[0016]The greatest feature of this invention is selection of a binding material. By using together the compound (three or more organic functions: T) which contains three or more epoxy groups at intramolecular to the compound (two organic functions: D) which contains two epoxy groups in intramolecular as a binding material, a "long chain branching structure object" can be introduced, a T/D ratio can be made to be able to increase, and a crystallization rate can be increased. This is presumed to be that on which the compound containing the epoxy group of three or more organic functions acts as "a crystallization nucleating additive of molecular size." Since the long chain branching structure object of this invention becomes possible [ increasing melt viscosity also by about 10 to 100 times by the "tangle effect" of a chain compared with the conventional line structure ], it serves as a compressed air or a sheet with little drawdown at the time of vacuum pressure sky shaping. By carrying out block copolymerization of the polyolefine (B-2) containing aromatic polyester (B1 ingredient) or carboxylic acid like the case of polyethylene terephthalate system polyester (a ingredient), In the compressed air of the time of sheet forming, and a sheet, or the heating immobilization at the time of vacuum pressure sky shaping (heat setting), a crystallization rate can be synthetically brought forward for the order of a second. Compound (D) b:100 to which epoxy-group-containing-compound d of this invention contains two epoxy groups in intramolecular - the compound (T) c containing the epoxy group of the number which exceeds 3 to 0 % of the weight and intramolecular: It is 0 to 100% of the weight of a mixture. The swell and melt viscosity of resin go abruptly up by the increase in latter (T). the wt. ratio (T/D ratio) of the latter/former -- usually -- 5 / 95 - 75/25 -- desirable -- 10 / 90 - 70/30 -- it is 25 / 75 - 50/50 still more preferably. A crystallization rate becomes quick by increase of a T/D ratio. An effect has few T/D ratios 5/95 or less, and

manufacture of polyester resin is difficult at 75/25 or more, and a gel fish eye carries out a byproduction to a sheet, and it does not become goods. A binding material masterbatch comprises d:10 to this mixture 50 weight section, and e:base 100 weight section. This mixture d has 15 to 20 preferred weight section. In ten or less weight sections, the binding material d has few effects of the masterbatch i, and becomes a high cost. Since the binding material d cannot manufacture the masterbatch f easily in 50 or more weight sections and it becomes easy to carry out the byproduction of the gel by a ligation reaction, it is not desirable.

[0017]There is the feature in this invention in using the binding material masterbatch f as dilution material using the base e, in order to prevent the local response of the binding material d leading to [ of the gel fish eye of a sheet ] a byproduction. As the base e, intrinsic viscosity 0.50 - polyethylene terephthalate system polyester of 0.90 dl/g, Condensation products (Eastman's pet G etc.), such as a collected polyethylene terephthalate system polyester mold-goods recycle thing, ethylene glycol, cyclohexane dimethanol, and terephthalic acid, toluene, benzene, xylene, etc. can be used. When a Plastic solid needs transparence, PET system polyester, toluene, benzene, xylene, etc. can be used. When a Plastic solid does not need transparence, polyethylene acrylate system resin (Japanese polyolefine, a stock, etc.) etc. can be used.

[0018]Although the rate of a compounding ratio of the binding material masterbatch f is usually one to 10 weight section to a:aromatic system saturated polyester 100 weight section, it is before and after [ desirable ] good 2 - 5 weight sections of distribution / mixing nature. With the increase in a ratio, MFR of the polyester block copolymer of A ingredient can be reduced, and melt viscosity can be increased.

[0019]Also in this invention, the desirable ligation reaction catalyst g is the complexes and those masterbatches i of metal salt of carboxylic acid. It has become clear by this invention that metal salt of carboxylic acid does not necessarily fit the purpose of manufacturing polyester of this invention, in single use. \*\* -- as the ligation reaction catalyst g, a complex is preferred. For example, as a 2 element-system catalyst. Lithium stearate/calcium stearate =20 / 80 - 50/100, sodium stearate/calcium stearate =20 / 80 - 50/100, manganese acetate/lithium stearate =20-50/100. Or it is manganese acetate/calcium stearate =20-50/100, etc. On the other hand, For example, as a ternary system catalyst. Lithium stearate / sodium stearate / calcium stearate =50/50/100, They are the compound catalysts g, such as lithium stearate / sodium acetate / calcium stearate =50/50/100 or lithium stearate / manganese acetate / calcium stearate =50/50/100, and the masterbatch i with those bases h.

[0020]There is another of the feature in this invention in using catalyst master batch i as dilution material using the base h, in order to prevent the local response of the catalyst g circumference leading to [ of the gel fish eye of a sheet ] a byproduction. As the base h, almost like the base e, intrinsic viscosity 0.50 - polyethylene terephthalate system aromatic polyester

of 0.90 dl/g, The collected aromatic polyester mold-goods recycle thing of a polyethylene terephthalate system, Condensation products (Eastman's pet G etc.), such as ethylene glycol, cyclohexane dimethanol, and terephthalic acid, polyethylene acrylate system resin (Japanese polyolefine, a stock, etc.), polyacrylate system resin (a copolymer is included), etc. can be used. When a Plastic solid needs transparence, PET system polyester, polyacrylate system resin (a copolymer is included), etc. can be used. When a Plastic solid does not need transparence, polyethylene acrylate system resin (Japanese polyolefine, a stock, etc.) etc. can be used. When not using the above-mentioned resin as the base h, catalytic activity is quiet and the lubricant effect can also use a certain calcium stearate. The percentage of calcium stearate may be 50 or more weight sections so much at a catalyst. Although this powdered compound catalyst has a technical problem of the workability of powder scattering, it is cheap and suitable for small-scale manufacture.

[0021]although the percentage of catalyst master batch i usually comprises g:5 to catalyst 15 weight section, and h:base 100 weight section -- desirable -- a catalyst -- it comprises catalyst g10 weight section and base h100 weight section still more preferably g:7.5 to 12.5 weight section. In five or less weight sections, the catalyst g has few effects of catalyst master batch i, and becomes a high cost. Since the catalyst g cannot manufacture the masterbatch i easily in 15 or more weight sections, and it is easy to carry out the byproduction of the gel by a ligation reaction and it becomes a cause of hydrolysis of resin at the time of a fabricating operation, it is not desirable. Although the amount of catalyst master batch i used is usually 0.25 to 10 weight section to a:aromatic saturated polyester 100 weight section, it is before and after [ desirable ] good 0.5 - the amount part of duplexs of distribution / mixing nature.

[0022]The manufacture by the reaction extrusion method of the block copolymer of this invention, In addition to the method of mixing simultaneously four ingredients of (1), (2), (3) and B1, or B-2, (1) It is also possible to mix with polyester component a, B1 aromatic-polyester ingredient, or B-2 polyolefin component beforehand under deaeration / drying, and to add (2) binding-material masterbatch f and (3) catalyst-master-batch i with a side supplying system after that. It is also possible to deaerate and dry the (1) ingredient a, to mix (2) binding-material masterbatch f and (3) catalyst-master-batch i, and to add B1 aromatic-polyester ingredient or B-2 polyolefin component with a side supplying system after that. It is also possible for an undried flake raw material to also use deaeration and drying, making it suitable.

[0023]As a reaction apparatus which carries out heat melting, the 2 axis reaction apparatus etc. of the self-cleaning nature used for manufacture of the polycondensation of a single screw extruder, a twin screw extruder, the 2 step-type extrusion machine of those combination and kneader Ruder, or PET system polyester resin can be used. Since especially the pyrogenetic-reaction method for manufacturing polyester resin of this invention is performed in a short time for about 2 to 10 minutes in an extrusion machine, as for ratio of length to diameter of a 2 axis

extrusion reaction machine, it is preferred that it is 30 to about 50, and 38 to about 45 are especially preferred. According to this invention, are based also on the performance of a reaction extrusion machine, but. general -- short time -- for example, preferably, it is the holding time for 1.5 minutes - 5 minutes preferably, and the molecular weight of saturated polyester goes abruptly up, block copolymerization is carried out to aromatic polyester or polyolefine, and desired block copolymerization generates especially for 1 minute - 10 minutes for 30 seconds - 20 minutes.

[0024]As for the above-mentioned reaction apparatus, it is preferred to use the thing which generally carried out hot air drying of a recovered PET bottle flake or the new polyester resin at 110-140 °C beforehand, and was lowered to the moisture content of 100-200 ppm, and the thing which dried by dehumidified air and lowered the moisture content to 50 ppm or less. Polyester resin usually adsorbs the humidity in the air, the moisture of 3,500-6,000 ppm (0.35 to 0.60 % of the weight) is included according to environmental moisture, and the purpose of this invention can be stably attained by performing the above drying processes. On the other hand, in using a recovered PET bottle flake or new article polyester resin as a raw material with un-drying, Make the vacuum line of a twin screw extruder into the oil-sealed type which is not a non-water seal type, and the degree of vacuum of the 1st - the 3rd vent Below  $13.3 \times 10^3$  Pa (100mmHg). Immediately after it lowers to  $0.66 \times 10^3$  Pa (5mmHg) still more preferably and polyester resin fuses below in  $2.6 \times 10^3$  Pa (20mmHg) preferably, it can attain by carrying out the vacuum deairing of the moisture and removing it during melting mixing.

[0025]The forming method of polyester of this invention can be enforced according to a precedence invention. That is, molding temperature can usually be about 260-290 °C, and it can fabricate on a sheet and a film. Since the pellet of polyester of this invention may adhere to a screw slot when the extrusion machine of molding equipment is a monopodium, lubricant like calcium stearate is mixable. 0.01 to lubricant 1 weight section can be used to pellet 100 weight section.

[0026]In polyester of this invention, manufacturing the block copolymer of the ingredient A, the ingredient B1, or ingredient B-2 with reaction equipment for launching. The metallic mold of a feed block method or a manifold method is used, from the exterior, additional supply of the ingredient B1 or ingredient B-2 can be carried out, it can fabricate on two-sort two-layer, two sorts of three layers, or a multilayer sheet, and a hot-forming object can newly be manufactured. In that case, a recovery pet's sheet layer is used for an inner surface so that foodstuffs may not be contacted directly.

[0027]In the extrusion molding of a heat-resistant sheet, the roll temperature in connection with heating immobilization is very important. 60-140 °C of 30-150 °C can usually be preferably used as a temperature of a touch roll and a chilled roll. moreover -- since a sheet is used once -- the time -- which heating immobilization -- being concerned -- roll temperature -- \*\*\*\*\* -- a touch

roll and a chilled roll -- 30-150 ° of temperature can usually be preferably used at 60-140 °.  
 [0028]90-140 ° of 60-150 ° can usually be preferably used for the compressed air of a sheet,  
 and the die temperature in vacuum pressure sky shaping.

[0029]

[Example]Next, this invention is explained in detail based on an example. Intrinsic viscosity (IV value), MFR (melt flow rate), a swell (degree of swelling), a molecular weight, and melt viscosity were evaluated about polyolefine or a block copolymer with aromatic system saturated polyester and a carboxylic acid group. Those valuation methods are as follows.

- (1) Intrinsic viscosity : about aromatic system saturated polyester, the mixed solvent of the same weight of 1,1,2,2-tetrachloroethane and phenol was used, and it measured at 25 ° with the Cannon-Fenske viscometer.
- (2) According to the conditions 20 of MFR:JIS K7210, it measured on the conditions of the temperature of 280 °, and 2.16 kg of load about aromatic system saturated polyester and a polyolefine polyester block copolymer composition. In addition, polyethylene is measured on 190 ° conditions and polypropylene is measured on the conditions of 2.16 kg of load at 230 °.
- (3) Swell : using the melt indexer for MFR, it discharged on the conditions of the temperature of 280 °, and 2.16 kg of load, and cut in the place which the sample gave 2.0 cm, the diameter of the place of 5.0 mm was measured from the lower end, and it computed by the following formula. The above-mentioned diameter was measured several times and the average value was adopted. The numerical value "2.095" of a following formula is a nozzle diameter of the melt indexer for MFR.  

$$\text{Swell (\%)} = \left[ \frac{\text{average-value} - 2.095 \text{ of a diameter}}{2.095} \right] \times 100$$
 (4) molecular weight: About polyester, it measured on condition of the following by the GPC method. (Main part) SYSTEM-21 by Showa Denko K.K., Shodex KF(column)-606M (2) sample, The reference side Hexa (solvent) fluoroisopropyl alcohol, (Column temperature) A part for 40 °, 20(injection rate) microl, and flow:0.6-ml/, (Polymer concentration) Measurement of 0.15-% of the weight and Shodex RI(detector)-74 and PMMA:Shodex M(molecular weight conversion standard)-75 (5) mechanical properties : Polymer with a press-forming machine. About 1 mm in thickness and about 3-mm press board were used on condition of application of pressure and water cooling for preheating and 60-atmosphere 30 seconds for 280 ° and 3 minutes. According to JIS K7113, the tensile test pierced the press board about 1 mm thick with the No. 2 dumbbell, and autograph DSS2000 of Shimadzu was used for it, and it performed it by a part for speed-of-testing/of 200 mm. According to an Izod impact test and JIS K7110, the press board about 3 mm thick was processed into the piece of the No. 2 mark, and it carried out about with the notch.
- (6) Melt viscosity : DynAlyserDAR-100 by Sweden REOLOGICA was used and the specimen

with a 2-cm angle x thickness of 2 mm was measured by adding the torsional oscillation between hot plates at 280 °C under a nitrogen atmosphere.

[0030][The example 1 of manufacture - 5:binding material masterbatches f1-f5] Product made from bell SUTORUFU 2 axis extruder, using the caliber of 43 mm, and ratio-of-length-to-diameter= 43 or 3-step water seal type vacuum suction -- the clear flake (the recovery article of a PET bottle.) of PET bottle Recycling of 50 weight sections and drying bag article 50 weight section of Eastman pet G 6763 (IV 0.73, density 1.27) which carried out hot air drying of intrinsic viscosity 0.75 dL/g, MFR56g/10 minutes at 120 °C for about 12 hours The preset temperature of 260 °C, Extruding by the screw speed of 200 rpm, 1st vent abbreviation-600mmHg, 3rd vent abbreviation-670mmHg, and automatic feed speed 30 kg/h. the ethylene glycol diglycidyl ether (the EPO light 40E of Kyoeisha Chemicals.) which is 2 organic-functions epoxy compound as a binding material from the 2nd vent holes Weight per epoxy equivalent 135 g/eq and light yellow fluid 15 weight section were poured in with the metering pump (binding material masterbatch f1:2 organic-functions / [ the example 1 of manufacture, and ] 3 organic-functions, and ratio T/D=0/100). Similarly to ethylene-glycol-diglycidyl-ether 75 weight section. Mixture of trimethylolpropane-triglycidyl-ether (EPO light 100MF [ of Kyoeisha Chemicals ], weight per epoxy equivalent 150 g/eq, light yellow fluid) 25 weight section of three organic functions 15 weight section was poured in with the metering pump (example 2 of manufacture, and binding material masterbatch f2:T/D=25/75). Similarly, mixture of trimethylolpropane-triglycidyl-ether 50 weight section of three organic functions 15 weight section was poured into ethylene-glycol-diglycidyl-ether 50 weight section with the metering pump (example 3 of manufacture, and binding material masterbatch f3:T/D=50/50). Similarly, mixture of trimethylolpropane-triglycidyl-ether 75 weight section of three organic functions 15 weight section was poured into ethylene-glycol-diglycidyl-ether 25 weight section with the metering pump (example 4 of manufacture, and binding material masterbatch f4:T/D=75/25). Similarly, mixture of trimethylolpropane-triglycidyl-ether 50 weight section of three organic functions 15 weight section was poured in with the metering pump (example 5 of manufacture, and binding material masterbatch f5:T/D=100/0). Five strands which flow out of the bore diameter of 3.5 mm of a die were water-cooled, the rotary cutter cut, and it was made the pellet. Subsequently hot air drying of each 100 kg of the obtained pellet was carried out at 120 °C at 140 °C for about 12 hours for about 1 hour, and it was kept to the dampproof bag.

[0031][The example 6 of manufacture - 7:catalyst master batch i1-i2] Product made from bell SUTORUFU 2 axis extruder, using the caliber of 43 mm, and ratio-of-length-to-diameter= 43 or 3-step water seal type vacuum suction -- the clear flake (the recovery article of a PET bottle.) of PET bottle Recycling of 50 weight sections of dry article 50 weight-section Eastman pet G 6763 (IV 0.73, density 1.27) for 10 minutes, The complex catalyst of lithium stearate 2.5 weight section, sodium stearate 2.5 weight section,

and calcium stearate 5.0 weight section was mixed with the tumbler (example 6 of manufacture, and complex catalyst master batch i1:Li/Na/Ca=25/25/50). Extruding by the preset temperature of 260 \*\*, the screw speed of 200 rpm, 1st vent abbreviation-630mmHg, 3rd vent abbreviation-730mmHg, and automatic feed speed 30 kg/h, five strands which flow out of the bore diameter of 3.5 mm of a dice were water-cooled, the rotary cutter cut, and it was made the pellet. Subsequently hot air drying of about 10 kg each of the obtained pellets was carried out at 120 \*\* at 140 \*\* for about 12 hours for about 1 hour, and they were kept to the dampproof bag. On the other hand, the complex catalyst of lithium stearate 2.5 weight section, sodium stearate 2.5 weight section, and calcium stearate 5.0 weight section was mixed and carried out with the tumbler (the example 7 of manufacture, powdered complex catalyst master batch i2:Li/Na/Ca=25/25/50).

[0032]the flake (a translucent recovery article.) of Example 1 - the example A1 of manufacture of the PET system polyester which differs in a T/D ratio, and its sheet forming - a 4 [A4] A-PET sheet Intrinsic viscosity 0.71 dl/g, MFR60g/undried elegance 100 weight section for 10 minutes, Powdered complex catalyst master batch i2(example of manufacture 7:Li/Na/Ca=25/25/50) 0.10 weight section and binding material masterbatch f1 (example of manufacture 1:T/D=0/100) 4.5 weight section were mixed with the tumbler. Twin screw extruder PCM-70 by IKEGAI CORP., the caliber of 70 mm, and ratio-of-length-to-diameter= 37 or 3-step oil-sealed vacuum suction are used, Extruding by the preset temperature of 280 \*\*, the screw speed of 100 rpm, 1st vent abbreviation-735mmHg, 2nd and 3rd vent abbreviation-750mmHg, and automatic feed speed 50 kg/h. Ten strands which flow out of the bore diameter of 2 mm of a dice were water-cooled, the rotary cutter cut, and it was made the pellet. Subsequently hot air drying of the obtained pellet was carried out at 120 \*\* at 140 \*\* for about 12 hours for about 1 hour, and it was kept to the dampproof bag. MFRs of the obtained masterbatch method PET system polyester A1 were 20g/10 minutes (example 1). The PET system polyester in which T/D ratios differ by the same operation was manufactured. f2 (example of manufacture 2:T/D=25/75) 4.0 weight section, f3 (example of manufacture 3:T/D=50/50) 7.0 weight section, and f4 (example of manufacture 4:T/D=74/25) 7.0 weight section were mixed and carried out with the tumbler as a binding material masterbatch, respectively. A3 was [ A4 of A2 of MFR of the obtained masterbatch method PET system polyester ] 2.1g/10 minutes (example 4) for 5.9g/10 minutes (example 3) for 18g/10 minutes (example 2), respectively.

[0033]Calcium stearate 0.2 weight section was mixed with the tumbler to these four sorts of pellet 100 weight sections. The single screw extruder GS-65 by IKEGAI CORP., caliber [ of 65 mm ], level extrusion T-die:250-mm width, 2-mm interval, and length 3 step-type polishing roll was used, and the thick sheet was fabricated. The transparent thick sheet (220 mm in width and 1-1.5 mm in thickness) was obtained with the preset temperature of 280 \*\*, the screw

speed of 60 rpm, automatic feed speed 30 kg/h, and the roll temperature of 30-50 \*\*. The thin cloudy weather which originates in A4 sheet at crystallization was observed. Although the result depended on DSC was shown in Table 1 (a part for elevating speed/of 10 \*\* under nitrogen), A-PET sheet of this invention found out that it was possible to make a degree of crystallinity increase also twice by the increase in a T/D ratio. transparent thick sheet A3 which manufactured the 170 \*\* isothermal crystallization time which is resin-molding temperature and the mean temperature of a chilled roll in Example 3 is about 30 seconds -- it was contrary and commercial A-PET sheet and resin were as late as tens of minutes.

表 1

実施例	路号	T/D 比	結晶化		融解		結晶化	結晶化		備考
			温度	熱量	温度	熱量		温度	熱量	
			(℃)	(J/g)	(℃)	(J/g)	(%)	(℃)	(J/g)	
1	A 1	6/100	130	- 27	246	35	5.82	193	- 36	
2	A 2	25/ 75	131	- 26	248	34	5.82	197	- 35	
3	A 3	50/ 50	123	- 26	247	40	10.0	198	- 39	
4	A 4	75/ 25	123	- 24	249	39	10.4	200	- 37	

[0034]Table 1

[0035]It manufactured with the compacting pressure of 6 atmospheres by the pressure-forming method, and the coffee cup-like thing was manufactured for the transparent thick sheet A2 with a thickness of 0.9 mm manufactured in example 5 Example 2 by rapid heating at the temperature of 150 \*\*. This transparent Plastic solid showed the heat resistance which bears microwave heating.

[0036]the clear flake (the recovery article of a PET bottle.) of PET bottle Recycling of Examples 6-7 [heat resistance sheet [ of the PET system polyester which carried out copolymerization of the PBT ] B1 - example of manufacture of B-2] \*\* Intrinsic viscosity 0.75 dl/g, MFR56g/undried elegance 100 weight section for 10 minutes, 35 weight sections of PBT1100N of Mitsubishi Rayon Co., Ltd. (example 6), Binding material masterbatch (f2:T/D=25/75) 7.5 weight section, Complex catalyst master batch (j2:Li/Na/Ca=25/25/50) 0.75 weight section, Or 100 weight sections (example 7) of PBT 1100N, binding material masterbatch (f2:T/D=25/75) 11 weight section, and complex catalyst master batch (j2:Li/Na/Ca=25/25/50) 0.75 weight section were mixed with the tumbler, respectively. The Ikegai twin screw extruder, the caliber of 70 mm, and ratio-of-length-to-diameter= 37 or 3-step oil-sealed vacuum suction are used, Extruding by the preset temperature of 280 \*\*, the screw speed of 100 rpm, 1st vent abbreviation-735mmHg, 2nd and 3rd vent abbreviation-750mmHg, and automatic feed speed 50 kg/h. Ten strands which flow out of the bore diameter of 2 mm of a dice were water-cooled, the rotary cutter cut, and it was made the pellet. Subsequently hot air drying of the obtained pellet was carried out at 120 \*\* at 140 \*\* for about

12 hours for about 1 hour, and it was kept to the dampproof bag. MFR of the obtained masterbatch method PBT-polyester block copolymer B1 - B-2 was as the design mostly for 20g of PBT35 weight sections (example 6)/10 minutes in 25g of PBT100 weight sections (example 7)/10 minutes, respectively. On the other hand, MFRs of the extrusion thing (comparative example 1) of PBT1100N resin pellet, and PET flake / PBT1100N=100 / 50 weight-section blend are 70g/10 minutes, 59g/10 minutes, respectively.

It completely differed from resin of this invention.

According to DSC measurement, PET/PBT=100 / 50 weight-section blend (comparative example 1) had the melting point divided into 214 ° (PBT) and 239 ° (PET), but resin PET/PBT=100 / 35 weight-section copolymer of this invention (example 6) showed only one melting point to 230 °. Resin of this invention has been easily fabricated at 260 ° on the transparent sheet.

[0037]the clear flake (the recovery article of a PET bottle.) of PET bottle Recycling of Example 8 [polyethylene polyester block copolymer E1 and multilayered sheet shaping] ° Intrinsic viscosity 0.75 dl/g, MFR56g/undried elegance 100 weight section for 10 minutes, lex pearl ET182 (carboxylic acid content polyethylene.) of Japanese Polyolefine 109, density 0.937, MFR280 °-melting point 30 weight sections of 98 °, binding material masterbatch (f2:T/D=25/75) 8.0 weight section, and complex catalyst master batch (i2:Li/Na/Ca=25/25/50) 0.75 weight section were mixed with the tumbler. IKEGAI 70 [ twin screw extruder PCM-], the caliber of 70 mm, and ratio-of-length-to-diameter= 37 or 3-step oil-sealed vacuum suction are used, Extruding by the preset temperature of 260 °, the screw speed of 100 rpm, 1st vent abbreviation-735mmHg, 2nd and 3rd vent abbreviation-750mmHg, and automatic feed speed 50 kg/h. Ten strands which flow out of the bore diameter of 2 mm of a dice were water-cooled, the rotary cutter cut, and it was made the pellet. Subsequently hot air drying of the obtained pellet was carried out at 120 ° at 140 ° for about 12 hours for about 1 hour, and it was kept to the dampproof bag. MFRs of the obtained masterbatch method polyethylene polyester block copolymer E1 were 3.5g/10 minutes.

[0038]The constituent of polyester A1[ polyethylene polyester block copolymer E1/ ] =50/50 weight section manufactured above: 100 weight sections and calcium stearate 0.2 weight section were mixed. A two-sort three-layer sheet was fabricated with the feed block type sheet forming device Made from °°. The main single screw extruder for block copolymer E1 : The caliber of 30 mm, ratio-of-length-to-diameter=38, the preset temperature of 270 °, the screw speed of 30 rpm, and commercial PET (the Unitika make, intrinsic viscosity 0.83 dl/g) -- the subsingle screw extruder:caliber of 25 mm of business, ratio-of-length-to-diameter=25, the preset temperature of 270 °, the screw speed of 10 rpm, T-die:250 mm width, the lip interval of 1.0 mm, a perpendicular style, a chilled roll: The level three-step warm water heating type was used. Gel and a fish eye have fabricated the 200-mm width which hardly carries out a

byproduction, and the two-sort three-layer sheet which has a high grade feeling with the white pearl length of 0.4 - 0.6-mm thickness by main speed-of-supply 6 kg/h and subspeed-of-supply 0.6 kg/h. There was no interlaminar peeling with a gummed cloth tape at the block copolymer E1-/polyester A1 (inside) and commercial PET (outside). Heating immobilization was carried out by passing a 110 ° heating roller for this sheet. The pressure-forming container bore 83 ° of the fill temperature of tofu or fermented soybeans.

[0039]the clear flake (the recovery article of a PET bottle.) of PET bottle Recycling of Example 9 [polypropylene polyester block copolymer P1 and multilayered sheet shaping] ° Intrinsic viscosity 0.75 dl/g, MFR56g/undried elegance 100 weight section for 10 minutes, ADTEX ER320P (carboxylic acid content polypropylene.) of Japanese Polyolefine 20, the density 0.91, MFR230 °-melting point 20 weight sections of 159 °, binding material masterbatch (f2:T/D=25/75) 8.7 weight section, and complex catalyst master batch (i2:Li/Na/Ca=25/25/50) 0.75 weight section were mixed with the tumbler. IKEGAI 70 [ twin screw extruder PCM-], the caliber of 70 mm, and ratio-of-length-to-diameter= 37 or 3-step oil-sealed vacuum suction are used, Extruding by the preset temperature of 280 °, the screw speed of 100 rpm, 1st vent abbreviation-735mmHg, 2nd and 3rd vent abbreviation-750mmHg, and automatic feed speed 50 kg/h. Ten strands which flow out of the bore diameter of 2 mm of a dice were water-cooled, the rotary cutter cut, and it was made the pellet. Subsequently hot air drying of the obtained pellet was carried out at 120 ° at 140 ° for about 12 hours for about 1 hour, and it was kept to the dampproof bag. MFRs of the obtained masterbatch method polypropylene polyester block copolymer P1 were 16.8g/10 minutes. Constituent:of polypropylene polyester block copolymer P1/polyester A1=50/50 weight section 100 weight section and calcium stearate 0.2 weight section which were manufactured above were mixed like said Example 8. A two-sort three-layer sheet was fabricated with the feed block type sheet forming device Made from °°. The 200-mm width in which gel and a fish eye hardly carry out a byproduction, and 0.4 - 0.6-mm thickness were translucent, and a two-sort three-layer sheet with a high grade feeling was obtained. The block copolymer P1-/polyester A1 (inside) and commercial PET (outside) did not have interlaminar peeling with a gummed cloth tape. Heating immobilization was carried out by passing a 110 ° heating roller for this sheet. The pressure-forming container bore 83 ° of the fill temperature of tofu or fermented soybeans.

[0040]

[Effect of the Invention]The heat-resistant cheap heat-resistant sheet heat-resistant [ transparent ] and opaque and Plastic solid of polyethylene terephthalate system polyester which are equal to heating of the container in which heating restoration of this invention is possible, and a microwave oven, Since the weak point on the physical properties of conventional pet resin is improved, a broad use is expectable besides containers, such as tofu and fermented soybeans, the lunch container of a convenience store, etc. The Plastic solid is

excellent in mechanical strengths, such as heat resistance and tensile strength.

It is useful as a common food container, a packing material, a packing material, a diaphragm, etc. in the field of daily needs, civil engineering and construction, electronic electrical machinery, a motor vehicle member, packing, etc.

Since the recovered PET bottle by which it is generated in large quantities can be used in large quantities and effectively as a prepolymer, it is socially useful. Even if it carries out incineration processing after use, it is rare for combustion calorific value to be low as compared with polyethylene or polypropylene, and to damage an incinerator, and generating of poisonous gas does not have it, either.

[0041]

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[Translation done.]